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10 Rec'd PCT/US 19 JUL 2004

REC'D 11 MAR 2003

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APPLICATION THAT MET THE REQUIREMENTS TO BE GRANTED A
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APPLICATION NUMBER: 60/351,146

FILING DATE: *January 23, 2002*

RELATED PCT APPLICATION NUMBER: *PCT/US03/01823*



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PROVISIONAL APPLICATION FOR PATENT COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53 (c).

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<input checked="" type="checkbox"/> Additional inventors are being named on the 1 separately numbered sheets attached hereto				
TITLE OF THE INVENTION (280 characters max)				
STABILIZED GRAIN SIZE REFRACTORY METAL POWDER METALLURGY MILL PRODUCTS				
CORRESPONDENCE ADDRESS				
Direct all correspondence to:				
<input checked="" type="checkbox"/> Customer Number	26486	Place Customer Number Bar Code Label here		
AND Type Customer Number here				
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Address				
Address				
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ENCLOSED APPLICATION PARTS (check all that apply)				
<input checked="" type="checkbox"/> Specification Number of Pages	12	<input type="checkbox"/> CD(s), Number		
<input checked="" type="checkbox"/> Drawing(s) Number of Sheets	4	<input checked="" type="checkbox"/> Other (specify)		
<input type="checkbox"/> Application Data Sheet. See 37 CFR 1.76		PROVISIONAL APPLICATION TRANSMITTAL - ADDITIONAL PAGE; PROVISIONAL APPLICATION COVER SHEET; AND RETURN RECEIPT POSTCARD		
METHOD OF PAYMENT OF FILING FEES FOR THIS PROVISIONAL APPLICATION FOR PATENT (check one)				
<input type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27.				
<input checked="" type="checkbox"/> A check or money order is enclosed to cover the filing fees		FILING FEE AMOUNT (\$) 160.00		
<input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge filing fees or credit any overpayment to Deposit Account Number:		03-2410 (Order No. 6160-1)		
<input type="checkbox"/> Payment by credit card. Form PTO-2038 is attached.				
The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.				
<input checked="" type="checkbox"/> No.				
<input type="checkbox"/> Yes, the name of the U.S. Government agency and the Government contract numbers are:				

Respectfully submitted,
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Date 1/23/02

REGISTRATION NO. 42,345
(if appropriate)

Docket Number: 6160-P76

USE ONLY FOR FILING A PROVISIONAL APPLICATION FOR PATENT

This collection of information is required by 37 CFR 1.51. The information is used by the public to file (and by the PTO to process) a provisional application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 8 hours to complete, including gathering, preparing, and submitting the complete provisional application to the PTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, Washington, D.C. 20231. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO Box Provisional Application, Assistant Commissioner for Patents, Washington, D.C. 20231.

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Additional Page

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EXPRESS MAIL LABEL NO. EV022273947US

FILING DATE: 01/23/02

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

PROVISIONAL APPLICATION

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INVENTION TITLE: STABILIZED GRAIN SIZE REFRACTORY METAL
POWDER METALLURGY MILL PRODUCTS

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TO: Commissioner for Patents
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Washington, D.C. 20231

Sir:

Your applicant(s), named above hereby request(s) acceptance
of the enclosed PROVISIONAL application entitled as stated above
pursuant to 35 U.S.C. 111(b).

60351445-012302

TITLE

STABILIZED GRAIN SIZE REFRACTORY
METAL POWDER METALLURGY MILL PRODUCTS

FIELD AND BACKGROUND OF THE INVENTION

1 This invention relates generally to metal mill products (and fabricated parts) made from powders of refractory metals including the elemental metals and their alloys and, more particularly to the use of oxide dopants for grain size stabilization in mill products and fabricated parts to be subjected to high temperature application usage and/or high temperature fabrication processes.

2 Users of refractory metals have had a long-standing interest in replacing tantalum with niobium. One driving force for such replacement of tantalum is price as well as the limited availability of tantalum. Many mill products involve high temperature exposure in fabrication and/or use. The high temperatures can cause grain growth. In various applications large grains, as a consequence of such grain growth, are detrimental to the performance of the material. This has been a limitation of niobium substitution for tantalum. Other limitations include lesser strength and hardness as-fabricated niobium and its alloys.

3 Currently, areas of interest include furnace parts, sintering trays and deep drawn cups as used for manufacturing synthetic diamonds. These products require material with small grain size. Furnace parts particularly require the material to have slow grain growth during service in order to prevent premature deterioration of the mechanical properties.

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Currently tantalum material with stabilized grain size, due to alloying additions or other artifacts, is used for wire or sheet. In one embodiment or state of interaction, SiO_2 is used as a grain stabilizer. The disadvantage of such a manufacturing method (resistance-sintering) for grain size stabilized tantalum powder metallurgy (P/M) material is that it is limited to a lot size of 30 pounds for tantalum and approximately 15 pounds for niobium. It is desirable to make lots sizes of up to 1000 pounds of tantalum and 500 pounds of niobium, respectively.

5 Current manufacturing methods for large P/M sheet sizes/strip length are not capable of providing large pieces of sheet or long coils of sheet with the same low level of oxygen content and good mechanical properties.

6 It is an object of this invention to provide a powder metallurgy (P/M) route to fabrication of refractory metals in large lots with low oxygen content and to provide resultant mill products with low oxygen content.

7 It is a further object of this invention to provide a P/M source for mill products and eventual mill products with a finer grain and a decreased grain growth than are achieved with ingot source materials.

8 These objects are applicable to refractory metals generally and more particularly to niobium and its alloys.

SUMMARY OF THE INVENTION

9 The objects set forth above as well as further and other objects and advantages of the present invention are achieved by the invention as described hereinbelow.

10 Grain growth inhibitors are added to niobium powder by blending inhibitors such as SiO_2 and Y_2O_3 prior to consolidation or as a residue of a de-oxidation process where magnesium is added to capture the oxygen from the niobium powder and form magnesium oxide during the de-oxidation process.

11 The powder is consolidated either by hot isostatic pressing (HIPing), extrusion or other thermomechanical working. Such methods of consolidation are capable of providing suitable P/M sheet bars with a weight of up to several hundred pounds. Subsequent thermomechanical processing of the P/M sheet bar is applied similarly to then P/M derived refractory metals as to metals from ingot sources.

12 The present invention inhibits grain growth in niobium P/M sheets during high temperature exposure. A low oxygen niobium powder (< 400 ppm, preferably < 200 ppm) is needed as a starting material. Powders with a higher content in oxygen cannot be consolidated to full density and/or will not yield good mechanical properties.

BRIEF DESCRIPTION OF THE DRAWINGS

13 Figure 1 is a flow chart showing a process of the present invention to create stabilized grain size powder; and

14 FIG. 2-4 are flow charts showing examples of consolidating steps to create products made of stabilized grain size powder.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

15 The metal powders with stabilized grain size of the present invention are produced via the following procedure as discussed in U.S. Patent 6,261,337 of Kumar.

16 As illustrated in FIG. 1, low oxygen niobium and grain growth inhibitor powders (for example SiO_2 or Y_2O_3) are blended to form low oxygen powder with grain size inhibitors. FIGS. 2-4 illustrate the consolidation steps with the master blend. The physical processes of blending and consolidating achieve a uniform distribution of grain growth inhibiting particles in the powder metal sheet bars. The powders are made by the process described in US 6,261,337 and as described herein.

17 These powders are blended to produce the desired alloy composition. The powders are then sealed in an evacuated can, heated to a desired temperature, and extruded such that the extrusion ratio is at least 8:1. This is done to completely consolidate the niobium powders and the included inhibitors. The can may be removed either just before or just after the rolling operation.

18 The above process can afford advantages of more stable grain size in the final material, more uniform material properties (such as ultimate tensile strength and hardness), lower manufacturing costs, better control of fiber size, and greater flexibility for alloy modifications and control of properties.

19

Niobium sheets produced from powder blends of niobium and grain inhibitors, for example silicon, were tested for grain growth, ultimate tensile strength, and hardness. The test results are presented in the table below.

Silicon (ppm)	1065°C @90 min (ASTM)	1150°C @180 min (ASTM)	1300°C @180 min (ASTM)	Ultimate Tensile Strength (KSI)	Hardness (VICKERS)
0	9.5	9.5	7.5	49.3	114
150	9.5	9.0	8.0	50.3	117
300	9.5	9.5	8.5	49.5	125
Nb I/M	5.5	<1	<1	32	72

20

P/M sheet with grain growth inhibitors, preferably silicon, of 0, 150, and 300 ppm were thermomechanical processed to a thickness of 0.015 inches and annealed at 1065.degrees.C for 90 minutes to produce grain sizes of approximately ASTM 9.5. Niobium sheet produced from ingot metallurgy (I/M) a grain size of approximately ASTM 5.5 under the same anneal heat treat conditions. The P/M and I/M test samples were subjected to additional annealing heat treatments at 1150.degrees.C for 180 minutes and 1300.degrees.C for 180 minutes. The P/M test samples yielded grain sizes greater than ASTM 7.0 compared to I/M test samples that yielded grain sizes coarser than ASTM 1. Additionally, the higher P/M Ultimate Tensile Strength of 49.3 KSI, 50.3 KSI, and 49.5 KSI and hardness of 114 VHN, 117 VHN, and 125 VHN are significant improvements over typical I/M material of Ultimate Tensile Strength of 32 KSI and hardness of 72 VHN. The fine grain sizes and improved tensile strength and hardness after heat treatment of the P/M material is a significant advantage,

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compared to I/M material, in applications where large amounts of deformation are required during fabrication, such as deep drawn diamond cups, or capacitor cans.

- 21 Alternatively, the blended powders may be isostatically pressed into a bar prior to canning and extrusion, as illustrated in FIG. 2. The advantage of this method would be to put a higher weight into the compact prior to extrusion to aid in consolidation and increase yield per extrusion.

- 22 Now returning to FIG. 1, niobium hydride powder is placed into a vacuum chamber, which also contains a metal having a higher affinity for oxygen, such as calcium or magnesium, preferably the latter. Preferably, the starting hydride powder has oxygen content less than about 1000 ppm. The chamber is then heated to the deoxidization temperature to produce a powder of niobium or alloy of niobium having a target reduced oxygen content of less than about 400 ppm preferably below 200 ppm and more preferably below 100 ppm. The magnesium, containing the oxygen, is then removed from the metal powder by evaporation and subsequently by selective chemical leaching or dissolution of the powder.

- 23 For example, a niobium powder with less than 400ppm oxygen can be produced by the deoxidization of niobium hydride under partial pressure of argon. Niobium hydride powder would be blended with 0.3 wt.-% magnesium and placed in a vacuum furnace retort, which is evacuated, and backfilled with argon. The pressure in the furnace would be set at 100 microns with Argon flowing and the vacuum pump running. The furnace temperature would be ramped to 650.degrees.C in approximately 50.degrees.C increments, held until temperature equalized, then ramped up to 950.degrees.C in approximately 50.degrees.C increments. When the temperature equalized at 950.degrees.C it would be held for about two hours. After such hold the furnace is shut down. Once the furnace cools its powder content is removed from the retort. The

magnesium, containing the oxygen, would then be removed from the metal powder by acid leaching to produce the resulting niobium powder having an oxygen content of less than 300 ppm.

24 As described above, in the process for producing formed powder metal products of niobium, the metal hydride powder is deoxidized to an oxygen content of less than about 400 ppm. The powder is consolidated to form a niobium or alloy product, having an oxygen content below about 400 ppm or 200 ppm or below 100 ppm, but for many powder metallurgy purposes between about 100 ppm and 150 ppm.

25 According to the present invention, a formed niobium product, having a stabilized grain size, may be produced from metal hydride powder by any known powder metallurgy techniques. Exemplary of these powder metallurgy techniques used for forming the products are the following, in which the steps are listed in order of performance. Any of the following single techniques or sequences of techniques may be utilized in the present invention:

26 cold isostatic pressing, sintering, encapsulating, hot isostatic pressing and thermomechanical processing;

27 cold isostatic pressing, sintering, hot isostatic pressing and thermomechanical processing;

28 cold isostatic pressing, encapsulating, hot isostatic pressing and thermomechanical processing;

29 cold isostatic pressing, encapsulating and hot isostatic pressing;

30 encapsulating and hot isostatic pressing;

31 cold isostatic pressing, sintering, encapsulating, extruding and thermomechanical processing;

32 cold isostatic pressing, sintering, extruding, and thermomechanical processing;

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- 33 cold isostatic pressing, sintering, and extruding;
- 34 cold isostatic pressing, encapsulating, extruding and thermomechanical processing;
- 35 cold isostatic pressing, encapsulating and extruding;
- 36 encapsulating and extruding;
- 37 mechanical pressing, sintering and extruding;
- 38 cold isostatic pressing, sintering, encapsulating, forging and thermomechanical processing;
- 39 cold isostatic pressing, encapsulating, forging and thermomechanical processing;
- 40 cold isostatic pressing, encapsulating and forging;
- 41 cold isostatic pressing, sintering, and forging;
- 42 cold isostatic pressing, sintering and rolling;
- 43 encapsulating and forging;
- 44 encapsulating and rolling.
- 45 cold isostatic pressing, sintering and thermomechanical processing;
- 46 mechanical pressing and sintering; and
- 47 mechanical pressing, sintering, repressing and resintering;
- 48 Other combinations of consolidating, heating and deforming may also be utilized.
- 49 The production of a formed niobium product having a stabilized grain size can be achieved by cold isostatic pressing of various kinds of known niobium powders to form a compact, followed by a hot

isostatic pressing (HIPing) step to densify the compact and then thermomechanical processing of the powder compact for further densification and completion of the bonding, as illustrated in FIG. 3. Preferably, niobium powder with grain size inhibitors would be cold isostatically pressed at 60,000 pounds/sq. in. and room temperature, into a compact with rectangular or, preferably, round cross section, then hermetically encapsulated and hot isostatically pressed (HIPed) at 40,000 lbs./sq. in. and 1300.degrees.C for four hours. The HIPed compact would be unencapsulated and converted to sheet or foil by thermomechanical processing steps.

50 A similar process, as illustrated in FIG. 4, of just cold isostatic pressing, sintering and thermomechanical processing using niobium powder having an oxygen content of less than 300 ppm can be conducted by cold isostatically pressing at 60,000 lbs./sq. in. into a bar shape preform. This preform would be sintered at 1500.degrees.C for two hours in a vacuum of less than about 0.001 Torr to yield a preform having a density of about 95% theoretical density (Th) and less than 400 ppm oxygen. The sintered preform would be converted into sheet and foil by thermomechanical processing steps.

51 Production of a formed niobium sheet or foil having a stable grain size by hot extrusion and thermomechanical processing can be made, using niobium powder having an oxygen content of less than 400 ppm as the starting powder. This powder can be hermetically encapsulated then extruded through a rectangular or, preferably, round die at 1000.degrees.C to produce an extruded product having oxygen content of less than 400 ppm. The extruded product can be converted to sheet or foil by the thermomechanical processing.

52 Niobium sheet or foil with oxygen content of less than 400 ppm can be produced by cold isostatic pressing, hot extrusion and thermomechanical processing. This compact made by cold isostatically pressing could be hermetically encapsulated then extruded at 1000.degrees.C to produce an extruded product with an

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oxygen content of about 300 ppm which can be converted into sheet and foil by thermomechanical processing steps.

53 Niobium products having stable grain size can be prepared by mechanical pressing, sintering, repressing and resintering. Niobium powder blend having oxygen content of less than 400 ppm can be utilized as the starting powder. It is placed in a die and mechanically pressed, using uniaxial pressure. The pressed tablet should be then sintered at 1500.degrees.C for two hours in a vacuum evacuated to less than about 0.001 Torr. The sintered tablet would then be repressed and resintered at 1500.degrees.C for two hours in a vacuum evacuated to less than about 0.001 Torr. The resintered tablet will have oxygen content of less than 400 ppm and be suitable for thermomechanical processing to produce a formed niobium product.

54 In one embodiment, a copper container is evacuated, filled with niobium powder, hermetically sealed, and extruded through a die to give a 10:1 extrusion ratio. The copper container is removed by acid treatment and the extruded bar is thermomechanically processed into a sheet form flat. In another embodiment, a steel container is evacuated, filled with the niobium powder, hermetically sealed and HIPed. The steel container is removed by machining and the HIPed piece is thermomechanically processed into a sheet form flat.

55 Anneals may be used to improve workability of the material in between two deformation steps or to adjust grain size and texture through recrystallization although a final anneal may not be necessary. When the powder is canned during the consolidation (usually to protect it from the environment at high temperature), the can will bond to the niobium.

56 In another embodiment, the process provides P/M sheets of large size (>100 pounds) having good mechanical properties and small stable grain size, capable of a higher yield than

conventional P/M processes for sheet manufacture, typically 50 pounds or less. Low oxygen niobium powder of less than 400 ppm, preferably less than 150 ppm, of non-spherical particles and sizing less than 150 microns FAPD (Fisher Average Particle Diameter), is provided per processes described herein. Powders with a higher content in oxygen cannot be consolidated to full density and/or will not yield good mechanical properties. The powder is consolidated either by HIPing (hot isostatic pressing) or by extrusion. Preferably, the powder is compacted into a coherent precursor form of at least 100 pounds with a density of 80-90% theoretical. The precursor density is brought to 95-100% theoretical. Both methods of consolidation are capable of providing suitable P/M sheet bars with a weight of up to several hundred pounds. Thermomechanical processing of the P/M sheet bar is similar to standard processes.

57

Numerous variations and modifications may obviously be made without departing from the present invention. Accordingly, it should be clearly understood that the forms of the present invention herein described are illustrative only and are not intended to limit the scope of the invention.

ABSTRACT OF THE DISCLOSURE

58 A powder metal (P/M) mill product and the method of fabrication such product made out of low oxygen (<400 ppm) niobium or alloys thereof, using oxide additive (such as MgO, SiO.sub.2, and Y.sub.2O.sub.3) for co-fabrication to achieve niobium grain size stabilization as required in high temperature applications. One such product is a sheet with small grain size containing oxide particles as grain size stabilizers. The product has good mechanical properties, low oxygen content in niobium fiber derivatives of the powder within the mill product and it is available as large pieces of sheet (lateral dimensions). The metal powder is consolidated to a sheet bar by different methods, which may weigh 50 pounds or more.

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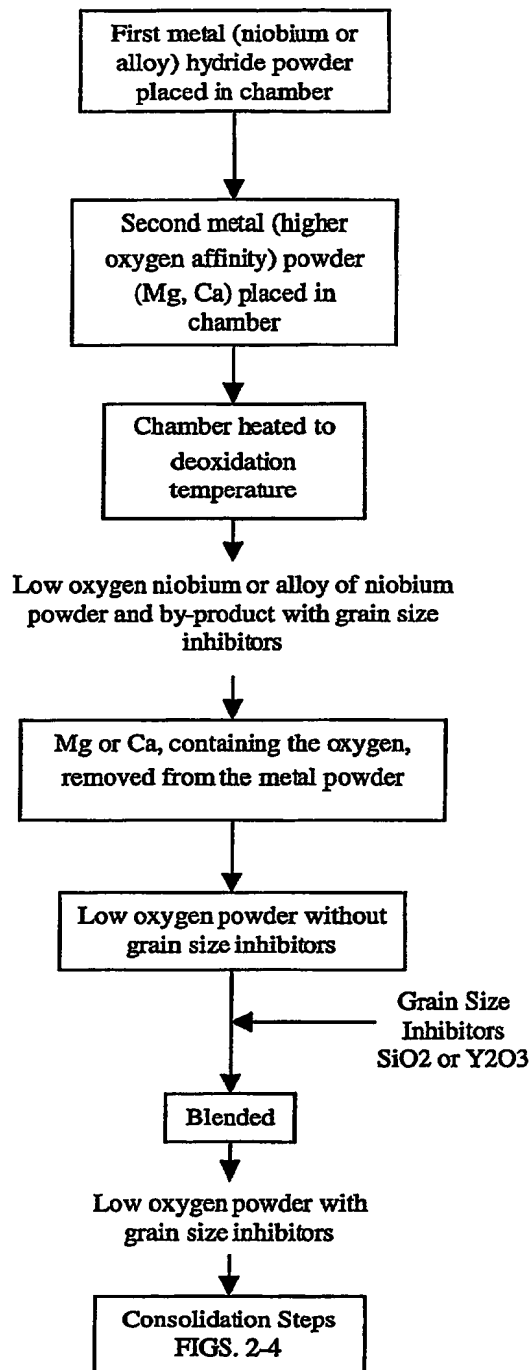


FIG. 1

Low oxygen powder with
grain size inhibitors

FIG 1

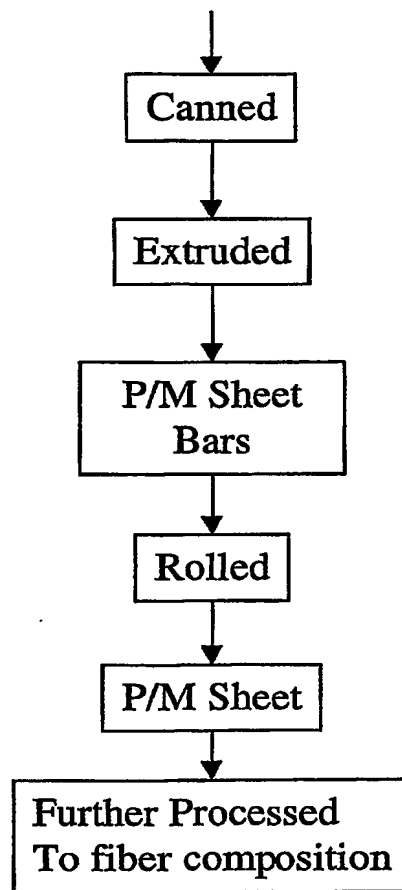


FIG. 2

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Low oxygen powder with
grain size inhibitors

FIG 1

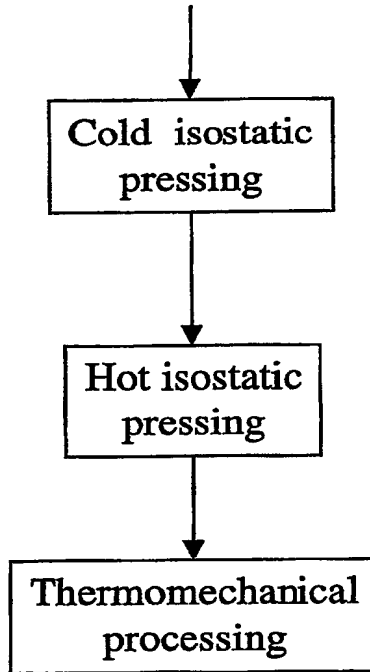


FIG. 3

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Low oxygen powder
with grain size inhibitors

FIG 1

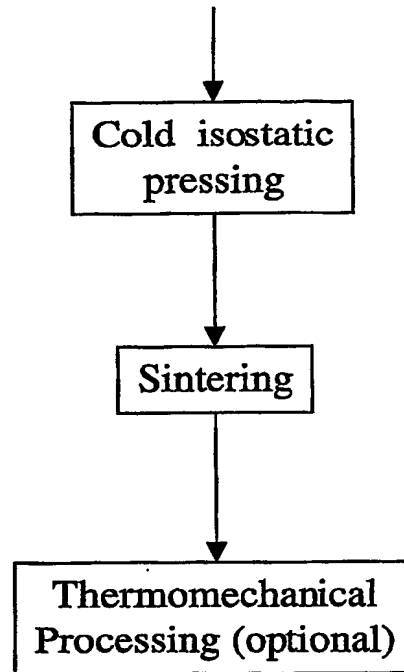


FIG. 4